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X-ray photoelectron spectroscopy study of high-k CeO$_2$/La$_2$O$_3$ stacked dielectrics

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This work presents a detailed study on the chemical composition and bond structures of CeO$_2$/La$_2$O$_3$ stacked gate dielectrics based on x-ray photoelectron spectroscopy (XPS) measurements at different depths. The chemical bonding structures in the interfacial layers were revealed by Gaussian decompositions of Ce 3d, La 3d, Si 2s, and O 1s photoemission spectra at different depths. We found that La atoms can diffuse into the CeO$_2$ layer and a cerium-lanthanum complex oxide was formed in between the CeO$_2$ and La$_2$O$_3$ films. Ce$^{3+}$ and Ce$^{4+}$ states always coexist in the as-deposited CeO$_2$ film. Quantitative analyses were also conducted. The amount of CeO$_2$ phase decreases by about 8% as approaching the CeO$_2$/La$_2$O$_3$ interface. In addition, as compared with the single layer La$_2$O$_3$ sample, the CeO$_2$/La$_2$O$_3$ stack exhibits a larger extent of silicon oxidation at the La$_2$O$_3$/Si interface. For the CeO$_2$/La$_2$O$_3$ gate stack, the out-diffused lanthanum atoms can promote the reduction of CeO$_2$ which produce more atomic oxygen. This result confirms the significant improvement of electrical properties of CeO$_2$/La$_2$O$_3$ gated devices as the excess oxygen would help to reduce the oxygen vacancies in the film and would suppress the formation of interfacial La-silicide also. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4902017]

I. INTRODUCTION

Rare-earth (RE) lanthanum oxide (La$_2$O$_3$) has attracted extensive attention as a promising candidate of gate dielectrics for next generation deca-nanoscale complementary metal-oxide-semiconductor (CMOS) applications. Lanthanum oxide has several outstanding features, such as high permittivity ($k \sim 27$), large energy gap ($5.8 \sim 6.55$ eV), and suitable conduction band offset with silicon ($> 2$ eV). However, there are some fundamental problems, such as hygroscopic nature, thermal instability, and poor interface properties with Si substrate, associated with the La$_2$O$_3$ film and need to be resolved in order to achieve better electrical and materials properties for high performance devices. In particular, its high amount of oxygen vacancies has been recognized as one of the key issues for the deteriorated material stability and device reliability. The large amount of oxygen vacancies in the bulk of La$_2$O$_3$ film would result in channel mobility degradation as well as threshold voltage shift. Additionally, oxygen vacancies can also induce the out-diffusion of substrate Si into the La$_2$O$_3$/Si interface and the bulk oxide as well. These effects will impede the realization of the smallest equivalent oxide thickness (EOT) due to the formation of low-k silicate layer. Several methods, such as element doping, thermal annealing, and the adoption of alloy forms of complex oxides, have been proposed to resolve these issues.

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Recently, a novel CeO$_2$/La$_2$O$_3$ gate stacked structure was proposed to control the level of oxygen vacancies in La$_2$O$_3$ film. The multivalent cerium oxides (in CeO$_2$ and Ce$_3$O$_4$ phases) have a smaller oxygen chemical potential and thus have low amount of oxygen vacancies. Cerium oxide can serve as a self-adapted oxygen reservoir. It supplies extra oxygen atoms to the La$_2$O$_3$ film so as to reduce the oxygen vacancies therein. It has already been confirmed that more favorable smaller oxygen chemical potential and thus have low amount of oxygen vacancies. Cerium oxide is a promising material for high performance oxygen sensors and solid oxide fuel cells. In this work, we conduct a detailed study on the bonding structure as well as the chemical composition at different depths of the as-deposited CeO$_2$/La$_2$O$_3$ stack by using x-ray photoelectron spectroscopy (XPS) measurements. By using Gaussian deconvolution technique, we made some further analyses on the distribution of Ce$^{3+}$ states and Ce$^{4+}$ states in CeO$_x$ layer so as to investigate the material interactions occurred at the CeO$_2$/La$_2$O$_3$ and La$_2$O$_3$/Si interfaces.

II. EXPERIMENT

Tungsten/CeO$_2$/La$_2$O$_3$ gate stack was deposited on n-type Si (100) substrates as follows. A La$_2$O$_3$ layer of about 5 nm thick and then a CeO$_2$ layer of about 2 nm thick were prepared by electron beam evaporation in an ultra-high vacuum chamber with a pressure of about $10^{-7}$ Pa. The tungsten gate electrode of about 3 nm thick was then deposited in situ using magnetron sputtering to avoid any moisture absorption and potential contamination. The film thicknesses were measured using an ellipsometer and confirmed with transmission electron microscopy (TEM) measurements. The chemical composition and the bonding structures of the as-deposited W/CeO$_2$/La$_2$O$_3$/Si gate stack at different depths were revealed by using x-ray photoelectron spectroscopy (XPS) measurement. The XPS machine is Physical Electronics Model PHI 5802 spectrometer with monochromatic Al K$_\alpha$ radiation energy of 1486.6 eV. Depth profiling was done by using Ar$^+$ sputtering at a rate of about 0.67 nm/min. The energy resolution is 0.1 eV.

III. RESULTS AND DISCUSSION

Fig.1 shows a typical atomic concentration profile of the stack we grew and a schematic diagram of the sample. With argon sputtering, we are able to register the composition change along the depth. As shown in Fig.1(b), in addition to the W, CeO$_2$, and La$_2$O$_3$ bulk layers, interfacial layers between the CeO$_2$/La$_2$O$_3$ and the La$_2$O$_3$/Si, indentified as, respectively, for the sputtering time between 11-16 min and 20-30 min, are also quite obvious. As will be shown later, CeO$_2$ and Ce$_3$O$_4$ co-exist in the CeO$_2$/La$_2$O$_3$ interface region. The reduction of CeO$_2$ phase can be understood with the following reaction:\(^{5,7}\)

$$4\text{CeO}_2 \leftrightarrow 2\text{Ce}_2\text{O}_3 + \text{O}_2.$$  \hspace{1cm} (1)

For sputtering time during $16 \leq t \leq 20$ min, it shows that the Ce content is very low and La dominates. This is the region of the bulk layer of La$_2$O$_3$ film. As sputtering into deeper, there is a region (for sputtering time between 20 to 30 min) notable La and Si contents which is attributed to the interfacial silicate layer at the La$_2$O$_3$/Si interface. This region seems to be quite thick but a TEM picture show that the La$_2$O$_3$/Si interface of this sample is quite sharp (see Fig. 1(c)). The interface silicate layer may be formed due to the recoil of La ions into the substrate and also the substrate oxidation from the decomposed oxygen during argon profiling.

Fig. 2 depicts a Ce 3d spectrum taken from the bulk CeO$_2$. The Ce 3d spectrum exhibits Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ spin-orbit doublet peaks, respectively, at 881.4 and 899.9 eV. The strong satellite peaks locating at around 885.7 eV and 904.2 eV are due to the Ce$^{3+}$ bonding of Ce$_3$O$_4$. These findings agree well with the data reported in the literatures.\(^{11-14}\) The present bulk Ce 3d spectrum
FIG. 1. (a) XPS depth profile of the as-deposited W/CeO$_2$/La$_2$O$_3$/Si sample revealed by using argon sputtering as a rate of about 0.67 nm/min. (b) Schematic diagram indicating the layered structure with transition region between CeO$_2$ and La$_2$O$_3$, and between La$_2$O$_3$ and Si. (c) Typical TEM picture of the cross-section of the sample.
indicates the co-existence of Ce$^{3+}$ and Ce$^{4+}$ bonding states. The recorded significant reduction of CeO$_2$ may be partially due to the reduction produced by the Ar sputtering.\textsuperscript{14,15} In addition, the as-deposited CeO$_2$ layer should also contain high amount of Ce$_2$O$_3$ phases. Nevertheless, depth profiling on the relative change of the Ce$^{3+}$ bonding states should still be able to reveal the additional reduction effect due to the La$_2$O$_3$ layer.\textsuperscript{16} Fig. 3 shows the Ce 3d XPS spectra taken from different depths, with sputtering time ranging from 9.5 min and 16 min. As the sputtering proceeds, slightly lower energy shift of the Ce 3d$_{5/2}$ peak from 881.4 eV to 881.2 eV was first observed for sputtering during 9.5 to 13 min. However, further sputtering would result in a higher energy shift instead (see Fig.3(b)). These phenomena are attributed, respectively, to the Ce-O-La bonding and the Ce-O-Si bonding. Unlike the bulk Ce-O-Ce bonding, the electron cloud on O would move closer to the Ce side in a Ce-O-La bonding because the Ce atom has slightly larger electronegativity ($\chi_{\text{Ce}} = 1.12$) than La atom ($\chi_{\text{La}} = 1.10$).\textsuperscript{5} Thus Ce 3d$_{5/2}$ has a slightly lower binding energy during the period $9.5 \leq t \leq 13$ min because of the formation of Ce-O-La complex bonding. As sputtering closer to the bulk of La$_2$O$_3$ (during the period of 13 to 16 min), the high-energy shift of the Ce 3d$_{5/2}$ peak may be due to the Si atoms in the La$_2$O$_3$. It was reported that Si can readily diffuse into the La$_2$O$_3$ via the oxygen vacancies.\textsuperscript{8} The forming of Ce-O-Si bonding causes the high-energy shift as Si has a much larger electronegativity ($\chi_{\text{Si}} = 1.9$).\textsuperscript{17}

Ce 3d XPS spectra are much more complicated than other high-k materials due to the hybridization between the 4f levels and the O 2p states.\textsuperscript{14} Both Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ levels are composed
of five different states, labeled as V and U refer, respectively, to the Ce 3d$\frac{3}{2}$ and Ce 3d$\frac{1}{2}$ spin-orbit components. By using Gaussian deconvolution technique, we found that the recorded spectra can be decomposed into nine peaks, namely, V$_0$ (881.05 eV), V$'$ (885.83 eV), U$_0$ (899.65 eV), U$'$ (904.3 eV) corresponding to Ce$^{3+}$ species, and V (882.52 eV), V$''$ (888.2 eV), V$'''$ (898.0 eV), U (901.13 eV), U$''$ (907.2 eV) corresponding to Ce$^{4+}$ species (see Fig.3(a)). These fitting results are consistent with other published reports$^{11,18,19}$ The decomposed spectra further confirm that both Ce$^{3+}$ and Ce$^{4+}$ states are co-existed in the CeO$_2$ layer. As shown in Fig. 3, when being sputtered deeper into the CeO$_2$/La$_2$O$_3$ interface, it is obvious that the peak of Ce$^{3+}$ state (V$_0$, V$'$, U$_0$, and U$'$) become stronger than that of the Ce$^{4+}$ states (V, V$''$, U, and U$''$).

To have a clearer picture on the amount of the CeO$_2$ reduction, we conduct a quantization analysis on ratio of Ce$^{3+}$ and Ce$^{4+}$ bonding composition. As mentioned, the V$_0$, V$'$, U$_0$, and U$'$ constitute the Ce$^{3+}$ states, the amount of this state should be governed by the total area of these peaks, i.e.

$$[\text{Ce}^{3+}] = U' + U_0 + V' + V_0$$

(2)

Similarly for Ce$^{4+}$ state, we have:

$$[\text{Ce}^{4+}] = U''' + U'' + U + V''' + V'' + V$$

(3)

The total fraction of the cerium in the Ce$^{3+}$ state (also referred to the degree of reduction) is:

$$[\text{Ce}^{3+}]\% = \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{3+}] + [\text{Ce}^{4+}]} \times 100\%$$

(4)

Noting that the U$''''$ state (-916 eV) for Ce$^{4+}$ was not taken into account due to the limited energy range in the experiment. It would introduce some errors for the figures given above.

Using the approach given above, we obtained the ratio of Ce$^{3+}$ content at different depths as indicated in Fig. 4. In the vicinity of the W/CeO$_2$ interface (t = 9.5 min), the percentage of Ce$^{3+}$ content is about 71.9% which is slightly smaller than the CeO$_2$ bulk of 77.6% (see the trace with sputtering time of 11 min). At the CeO$_2$/La$_2$O$_3$ interface, the Ce$^{3+}$ content increases to over 80%. It is noted that the smallest percentage of Ce$^{3+}$ is still over 71.9%. The high Ce$^{3+}$ content should be partially due to the artifact produced by Ar sputtering during XPS measurements. It was reported that Ar or ion beam can result in CeO$_2$ reduction.$^{14,15}$ A large amount of CeO$_2$ should also be formed during the deposition. Further increase of Ce$^{3+}$ content as sputtering closer to the CeO$_2$/La$_2$O$_3$ interface indicates that the lanthanum oxide had facilitated the reduction of cerium oxide because of the larger amount of oxygen vacancies in the La$_2$O$_3$ film.$^{5,18}$

Figure 5 shows the La 3d spectra taken from different locations of the W/CeO$_2$/La$_2$O$_3$ by sputtering. The La 3d$_{3/2}$ spectra demonstrate a double peak structure with main peak energy of 851.0 eV and satellite peak energy of 855.6 eV.$^{1}$ As being sputtered deeper into the film, the doublet shows a slight high-energy shift to 851.3 eV. This shift is attributed to the presence of the Ce-O-La bond in the CeO$_x$-La$_2$O$_3$ mixture layer and that agrees with the Ce 3d result as given above. After 13 min sputtering, i.e. closed to the bulk La$_2$O$_3$, the La 3d spectra shift to higher energy side because of the present of Si neighbors for the La bonding. In the La$_2$O$_3$/Si interface region, with sputtering time between 20 to 30 min, the main peak of La 3d$_{3/2}$ shifts to even higher energy at 852.6 eV and the intensity of the satellite peak becomes weaker indicating more silicate bonding (La-O-Si) formed at the interface. No obvious satellite peak becomes corresponding to La-Si bonding can be detected at the La$_2$O$_3$/Si interface.

Fig. 6(a) and 6(b) depict the Si 2s XPS spectra and Gaussian deconvolution results for the as-deposited W/CeO$_2$/La$_2$O$_3$/Si sample. The peak at 150.5 eV is due to the Si-Si bonds and the high-energy shifts of the peaks are attributed to the La-rich lanthanum silicate or the Si-rich lanthanum silicate. The Si 2s peak shifts to 153.8 eV after being sputtered for 20 min. It represents the SiO$_2$ bonding at the SiO$_2$/Si interface. In order to further study the effect of CeO$_2$ on the La$_2$O$_3$/Si interface, we compare the Si 2s spectra with the sample without CeO$_2$ capping. Detailed comparison and peak decomposition at three different locations, corresponding to the bulk La$_2$O$_3$, the La-rich silicate near La$_2$O$_3$/Si interface, and the Si-rich silicate near La$_2$O$_3$/Si interface, are
FIG. 4. Deconvoluted Ce 3d spectra by using Gaussian decomposition. The percentages of Ce\(^{3+}\) content indicated in the figure were calculated from the total area of peaks corresponding to Ce\(^{3+}\) ions (i.e., \(V_0\), \(V\)-, \(U_0\), and \(U\)-peaks) as a fraction of total peak area corresponding to both Ce\(^{3+}\) and Ce\(^{4+}\) ions.

FIG. 5. XPS spectra of La 3d taken at different depths for the as-deposited La\(_2\)O\(_3\) film in the CeO\(_2\)/La\(_2\)O\(_3\) gate stack corresponding to sputtering time: (a) 10.5–13 min (CeO\(_2\) bulk), (b) 13–30 min (CeO\(_2\)/La\(_2\)O\(_3\) interface, bulk La\(_2\)O\(_3\), and La\(_2\)O\(_3\)/Si interface).
FIG. 6. Comparison of the Si 2s XPS spectra in the CeO$_2$/La$_2$O$_3$/Si and La$_2$O$_3$/Si stacks: (a) Si 2s XPS spectra of the CeO$_2$/La$_2$O$_3$/Si stack at different depths; (b) Si 2s XPS spectra of the La$_2$O$_3$/Si stack at different depths; Comparison of Si 2s spectra with Gaussian peak decomposition near the La$_2$O$_3$ surface or the CeO$_2$/La$_2$O$_3$ interface (c), near the La$_2$O$_3$/Si interface (d), and close to the Si substrate (e). The markers are raw data, the broken curves are the Gaussian deconvolution results, and the solid lines represent the spectra synthesis from deconvoluted peaks.

shown in Fig. 6(c) to (e). For the Si 2s interface spectrum near the bulk side of La$_2$O$_3$ of the CeO$_2$/La$_2$O$_3$ sample, i.e., at sputtering time $t = 20$ min, an additional peak with energy of 153.8 eV corresponding to the Si-O-Si phase is observed. It suggests that oxidation of La-Si bonding at the interface had been taken place. For sample without CeO$_2$, no Si-O bonding is observed, instead, a weak La-Si bonding signal at around 148.4 eV was found at the La$_2$O$_3$/Si interface. It implies that the additional oxygen provided by the capping CeO$_2$ film would promote silicon or La-Si oxidation. This reaction would help to improve the quality of La$_2$O$_3$/Si interface layer and thus leads to better electrical characteristics of the devices.

The conjectures given above are further confirmed with the O 1s spectra as shown in Fig. 7. As shown in Fig. 7(a), several different kinds of bonding were observed as sputtering from CeO$_2$ layer (9.5 min) to near silicon substrate (27 min). Along the depth direction, we can observe first
FIG. 7. (a) O 1s photoelectron spectra taken at different locations of the as-deposited CeO$_2$/La$_2$O$_3$/Si stack; (b) deconvoluted results of the O 1s photoelectron spectra at different depths corresponding to sputtering time at 11 min, 13.5 min, 16 min, 20 min, and 27 min. The markers represent the raw data, the broken curves are the Gaussian deconvolution results, and the solid lines are the spectra synthesized from deconvoluted peaks.
a slight low-energy shift from 530.5 eV to 530.3 eV (9.5 \leq t \leq 13.5 \text{ min}) due to appearance of La-O-La (with O 1s energy of 528.8 eV) in the CeO$_2$ film, and then a high-energy shift to 531.0 eV (after sputtering time >13.5 \text{ min}) because of the formation of silicate. Fig. 7(b) also depicts the decomposed O 1s peaks at different depths. For \( t = 11 \text{ min} \), the O 1s spectra of the CeO$_2$ layer can be decomposed into three peaks corresponding to Ce$^{3+}$ (530.6 eV) or Ce$^{4+}$ (529.8 eV and 531.8 eV).\cite{17} For \( t = 13.5 \text{ min} \), the broad O 1s peak is constituted by both Ce-O bonding and La-O bonding. It further verifies that cerium-lanthanum complex oxide was formed. As etching closer to the CeO$_2$/La$_2$O$_3$ interface, the intensities of Ce (III)-O bonding and La-O bonding become stronger while the intensity of Ce (IV)-O bonding decreases, indicating more reduction of Ce$^{4+}$ to Ce$^{3+}$ near the La$_2$O$_3$ film. This result agrees with the [Ce$^{3+}$] fraction as calculated from the Ce 3d spectrum as shown in Fig. 3. At the La$_2$O$_3$/Si interface (t = 20 min), the O 1s spectrum can be deconvoluted into La-O-Si (530.6 eV) and Si-O (531.5 eV). It confirms that the excess oxygen from CeO$_2$ layer can cause the interface oxidation and that is consistent with the Si 2s spectra given in Fig. 6.

IV. CONCLUSION

The chemical composition and the bond structure of the CeO$_2$/La$_2$O$_3$/Si stack at different depths have been studied in detail by using x-ray photoelectron spectroscopy (XPS) measurements. Gaussian deconvolutions of the Ce 3d, Si 2s, and O 1s spectra at different depths reveal the material interactions in this stacked structure. Results indicate that cerium-lanthanum complex oxide was formed at the CeO$_2$/La$_2$O$_3$ interface. Ce$^{3+}$ and Ce$^{4+}$ states always co-existed and the amount of Ce$_2$O$_3$ was over 70\% in the as-deposited CeO$_2$ film which may be partially due to the reduction effect due Ar sputtering during XPS measurements. Near the CeO$_2$/La$_2$O$_3$ interface, the Ce$_2$O$_3$ content increases to over 80\% indicating the serious oxygen deficiency in La$_2$O$_3$ film which has caused the reduction of cerium oxide to lower oxidation state. Different to the La$_2$O$_3$ sample without the CeO$_2$ capping, the CeO$_2$/La$_2$O$_3$ stack exhibits interface oxidation at the La$_2$O$_3$/Si interface due to the present of excess oxygen from the capping CeO$_2$ layer. These observations explained the improved electrical characteristics of MOS transistors using CeO$_2$/La$_2$O$_3$ as the gate dielectrics reported earlier.\cite{9}

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